NEW YORK UNIVERSITY

CHEMISTRY DEPARTMENT

UNIVERSITY HEIGHTS

Contract No. NSG 76-60

Summary of work done in the period

November 1, 1964 to April 30, 1965

THEORETICAL STUDY OF ATOMIC AND MOLECULAR GASES

AND THEIR REACTIONS

IN THE UPPER ATMOSPHERE

Submitted to the National Aeronautics and Space Administration, Washington, 25, D. C. The report contains a brief summary of the work done during the period November 1, 1964 to April 30, 1965.

Roop C. Sahni
Project Director

PERSONNEL

Dr. R. C. Sahni   Chief Investigator and
Project Director

Dr. C. Donald La Budde   Research Scientist

Dr. Franz-Joseph Heinen   Assistant Research Scientist

Dr. E. J. De Lorenzo   Assistant Research Scientist

Dr. D. C. Jain   Assistant Research Scientist

Mr. B. C. Sawhney   Assistant Research Scientist

Mr. O. P. Anand   Research Assistant

Mr. M. D. Sawhney   Research Assistant

INTRODUCTION

In the previous report it was stated that we had extended the computer programs to include 3s and 3p functions along with 1s, 2s and 2p functions for the calculation of the electronic wave functions and total energies of diatomic molecules. We also stated in that report that most of the work done upto date was applied to the equilibrium distances of the ground, ionized and excited states of diatomic molecules. We have now extended this work to a number of internuclear distances of these molecules to obtain the potential energy curves. Furthermore, we have also built up programs where, in addition to the usual treatment, we have varied the screening constants of the basic function to obtain the best LCAO MO's. So far the best LCAO MO work is confined to 1s, 2s and 2p functions. Attempt is now being made to include 3s, 3p and 3d functions in the calculation of the best LCAO MO's. We hope to describe these results in the coming report. The work during the last six months got a special impetus due to time allotted to us on IBM 7094 computer of the Institute for Space Studies, 475 Riverside Drive, New York, New York. The excellent facilities and co-operation of the personnel of the Institute have made it possible for us to make good progress in this work.

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Work carried out during the above period can be given under the following headings:

(1) Computation of the Wave Functions and Total Energies of the Different Electronic States of Isoelectronic N_2 and CO Molecules with A View To Predict Their Equilibrium Distances.

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(3) Development of the Computer Programs To Calculate the Best LCAO MO's for Homopolar Diatomic Molecules.

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(1) COMPUTATION OF THE WAVE FUNCTIONS AND TOTAL ENERGIES OF THE DIFFERENT STATES OF THE ISOELECTRONIC N_2 AND CO MOLECULES WITH A VIEW TO CALCULATE THEIR EQUILIBRIUM DISTANCES

by B. C. Sawhney, O. P. Anand and R. C. Sahni

The automatic homo- and hetero programs have been used to calculate the wave functions and total energies of six electronic states of N_2 and seven states of CO at a number of internuclear distances to calculate their equilibrium distances. The programs used Slater orbitals as basic functions. The calculated equilibrium distances are the first approximation to the more exact work, where the screening constants are varied, now in progress. The computed energy values are given in Table I and Table II and the calculated equilibrium distances from the above data are given in Table III and Table IV along with the observed values.

(2) PREDICTION OF THE GROUND, IONIZED AND EXCITED STATES OF THE NF MOLECULE FROM THE QUANTUM MECHANICAL TREATMENT OF THE ISOELECTRONIC O_2 AND NF MOLECULES

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TABLE I

TOTAL ENERGIES OF DIFFERENT STATES OF N_2 MOLECULE AT VARIOUS INTERNUCLEAR DISTANCES

$\alpha = 6.6675 \qquad \beta = \gamma = \delta = 1.95$

R	$N_2\ ^1\Sigma_g$ 2.0675	$N_2\ ^3\Sigma_u$ 2.4435	$N_2\ ^3\Pi_u$ 2.1699	$N_2\ ^3\Pi_g$ 2.2910	$N_2^+\ ^2\Sigma_g$ 2.1094	$N_2^+\ ^2\Sigma_u$ 2.0315
1.90	-108.50664330	-108.14582634	-108.01993752	-108.17588425	-107.93795967	-107.78673363
1.95	-108.53651524	-108.20601940	-108.05690098	-108.22309208	-107.97514248	-107.81339931
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2.4435	-108.52298260	-108.42868519	-108.08627224	-108.35072613	-108.02801609	-107.76351261
2.1699	-108.58127213	-108.36924934	-108.12618828	-108.36681107	-108.05045509	-107.84259796
2.2910	-108.56578846	-108.40950012	-108.12010384	-108.34996712	-108.05101776	-107.81772614
2.1094	-108.58020973	-108.33788681	-108.11937714	-108.31785011	-108.04117966	-107.84600639
2.0315	-108.56740284	-108.28355122	-108.09807873	-108.28082180	-108.01760006	-107.83875751

TABLE II – TOTAL ENERGIES OF DIFFERENT STATES OF CO MOLECULE AT VARIOUS INTERNUCLEAR DISTANCES

R	$^3\Pi$ (CO)	$^3\Delta$ (CO)	$X\,^1\Sigma$ (CO)	$c\,^2\Sigma$ (CO$^+$)	$X\,^2\Sigma$ (CO$^+$)	$A\,^2\Pi$ (CO$^+$)	$B\,^2\Sigma$ (CO$^+$)
1.90	-111.97424603		-115.23902798		-111.78087902		-111.42243862
1.95	-112.01778221	-111.89608574	-112.29486847		-111.81227303		-111.45487213
2.00	-112.05291748	-111.94694138	-112.31681442	-110.78995514	-111.83583450		-111.47964859
2.05	-112.08070755	-111.99008560	-112.33207321	-110.83036613	-111.85273170		-111.49787331
2.10	-112.10238266	-112.02656937	-112.34168434	-110.86468315	-111.86396408	-111.78398895	-111.51057243
2.15	-112.11864948	-112.05714130	-112.34640408	-110.89357662	-111.87039852	-111.80711269	-111.51859188
2.20	-112.13039207	-112.08272362	-112.34704590	-110.91785812	-111.87287712	-111.82560539	-111.52266884
2.25	-112.13831711	-112.10388184	-112.34418869	-110.93803787	-111.87201118	-111.84011650	-111.52353897
2.30	-112.14287376	-112.12103271	-112.33818436	-110.95444298	-111.86835098	-111.85105324	-111.52169418
2.35	-112.14478207	-112.13495731	-112.32978153	-110.96789074	-111.86255360	-111.85912228	-111.51773167
2.40	-112.14426422	-112.14583397	-112.31918526	-110.97831154	-111.85496330	-111.86448479	-111.51213264
2.45	-112.14194870	-112.15419960	-112.30690193	-110.98631859	-111.84608641	-111.86773300	-111.50533485
2.50	-112.13806438	-112.16026592	-112.29314895	-110.99185658	-111.83613110	-111.86907482	-111.49762440
2.55	-112.13303375	-112.16435432	-112.27814102	-110.99520874	-111.82550240	-111.86875916	-111.48933601
2.60	-112.12682152	-112.16669083	-112.26219940	-110.99636650	-111.81435966	-111.86703491	-111.48070717
2.65	-112.11972904	-112.16752929	-112.24554920	-110.99544621	-111.80296421	-111.86421871	-111.47183132
2.70	-112.11220027	-112.16697788	-112.22819042	-110.99233150	-111.79129505	-111.86032772	-111.46261311
2.75		-112.16510201	-112.21033096	-110.98709869	-111.77958488	-111.85550777	-111.45306969
2.80		-112.16249371	-112.19238758	-110.98032475	-111.76816273	-111.85039997	-111.44330311
2.85		-112.15889549	-112.17424583	-110.97213364	-111.75688362	-111.84469986	-111.43299675

TABLE III

EQUILIBRIUM DIATANCES (Re) OF THE VARIOUS ELECTRONIC
STATES OF N_2 MOLECULE IN ATOMIC UNITS (a.u.)

STATE	EQUILIBRIUM DISTANCE		
	CALCULATED	OBSERVED	% ERROR
N_2 X $^1\Sigma_g^+$	2.15	2.0675	3.99%
A $^3\Sigma_u^+$	2.48	2.4435	1.49%
$^3\Pi_u$	2.20	2.1699	1.39%
$^3\Pi_g$	2.34	2.2910	2.14%
N_2^+ X $^2\Sigma_g^+$	2.23	2.1094	5.72%
B $^2\Sigma_u^+$	2.11	2.0315	3.86%

TABLE IV

EQUILIBRIUM DISTANCES OF THE VARIOUS ELECTRONIC STATES
OF CO MOLECULE IN ATOMIC UNITS (a.u.)

STATE	EQUILIBRIUM DISTANCE		
	CALCULATED	OBSERVED	% ERROR
CO X $^1\Sigma^+$	2.18	2.132	2.25%
a $^3\Pi$	2.365	2.2853	3.49%
d $^3\Delta$	2.65	2.5888	2.36%
CO^+ X $^2\Sigma^+$	2.21	2.1072	4.87%
A $^2\Pi_1^+$	2.51	2.3502	6.79%
B $^2\Sigma^+$	2.24	2.2085	1.42%
c $^2\Sigma^+$	2.60	——	——

$$\text{NF } X\ ^3\Sigma : \quad 1\sigma^2 \quad 2\sigma^2 \quad 3\sigma^2 \quad 4\sigma^2 \quad 5\sigma^2 \quad \pi_x^2 \quad \pi_y^2 \quad \pi_x^* \quad \pi_y^*$$

$$\text{NF } ^1\Delta : \quad 1\sigma^2 \quad 2\sigma^2 \quad 3\sigma^2 \quad 4\sigma^2 \quad 5\sigma^2 \quad \pi_x^2 \quad \pi_y^2 \quad \pi_x^{*2}$$

$$\text{NF}^+\ ^2\Pi : \quad 1\sigma^2 \quad 2\sigma^2 \quad 3\sigma^2 \quad 4\sigma^2 \quad 5\sigma^2 \quad \pi_x^2 \quad \pi_y^2 \quad \pi_x^*$$

$$\text{NF}^+\ ^4\Pi : \quad 1\sigma^2 \quad 2\sigma^2 \quad 3\sigma^2 \quad 4\sigma^2 \quad 5\sigma^2 \quad \pi_x^2 \quad \pi_x \quad \pi_x^* \quad \pi_y^*$$

The computed total energies of the states of O_2 are given in Table V and those of NF in Table VI. The calculated equilibrium distances from the above data are given in Table VII for states of O_2 molecule along with observed data.

The predicted equilibrium distances of the states of NF along with excitation and ionization energies are given in Table VIII. The above results are preliminary. A more complete study using the best MO's (where both the linear coefficients and orbital exponents are varied) is under way. The complete results will be described in the next report.

(3) **DEVELOPMENT OF THE COMPUTER PROGRAM FOR THE VARIATION OF THE SCREENING CONSTANTS OF THE 1s, 2s AND 2p ATOMIC ORBITALS TO OBTAIN BEST LCAO MO'S FOR THE DIFFERENT ELECTRONIC STATES OF DIATOMIC HOMOPOLAR MOLECULES**
by R. C. Sahni and C. D. La Budde

It was stated in the previous report that an automatic program has been built up which computes wave functions and total energies of homopolar diatomic molecules. This program can compute six to seven states of the same molecule in 3 - 4 minutes in a single run. The program uses fixed screening constants as an input data. It is usual to use Slater screening constants. In order to get the best wave functions and total energies it is necessary to vary the screening constants to optimize the total energy. Such a program has been constructed and a number of states of N_2 and O_2 have been computed. The total energies of these states are given in Table IX along with those computed by using only Slater's screening constants. In all cases best LCAO MO's give better results.

(4) **DEVELOPMENT OF THE COMPUTER PROGRAMS FOR THE VARIATION OF THE SCREENING CONSTANTS OF THE 1s, 2s AND 2p ATOMIC ORBITALS TO OBTAIN BEST LCAO MO'S FOR THE DIFFERENT ELECTRONIC STATES OF DIATOMIC HETEROPOLAR MOLECULES**
by C. D. La Budde and R. C. Sahni

An 'auto vary' program has been built up which varies the screening constants of the different atomic orbitals of heteropolar molecules till the optimized energy is obtained. This program is more complicated than a similar program for homopolar molecules. This program has been used to calculate the

TABLE V
TOTAL ENERGIES OF STATES OF O_2 MOLECULE AT VARIOUS R

$\alpha = 7.6528 \qquad \beta = \gamma = \delta = 2.275$

R	$O_2 \ ^3\Sigma_g^-$	$O_2 \ ^1\Delta$	$O_2 \ ^4\Pi$	$O_2 \ ^2\Pi$
2.00	-149.02007866	-148.93554115	-148.48109627	-148.66397476
2.05	-149.04732704	-148.96336937	-148.53122520	-148.68243599
2.10	-149.06742668	-148.98403314	-148.57303238	-148.69430542
2.15	-149.08137894	-148.99849701	-148.60758781	-148.70056343
2.20	-149.09014702	-149.00779533	-148.63587379	-148.70213509
2.25	-149.09440804	-149.01255989	-148.65863800	-148.69966125
2.30	-149.09491158	-149.01353455	-148.67663765	-148.69385719
2.35	-149.09214592	-149.01122856	-148.69046211	-148.68519783
2.40	-149.08661842	-149.00615120	-148.70061684	-148.67414665
2.45	-149.07877731	-148.99873161	-148.70763397	-148.66114235
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2.55	-149.05746460	-148.97822571	-148.71364784	-148.63051987
2.60	-149.04456902	-148.96571732	-148.71332932	-148.61343002
2.65	-149.03048897	-148.95200157	-148.71114159	-148.59544945
2.70	-149.01558113	-148.93743706	-148.70748901	-148.57689476
2.28170	-149.09510422	-149.01355362	-148.67054176	-148.69631004
2.29705	-149.09498596	-149.01357651	-148.67571831	-148.69429779
2.12163	-149.07416344	-148.99098587	-148.58880615	-148.69765663
2.61025	-149.04183960	-148.96305084	-148.71307755	-148.60987091

TOTAL ENERGIES OF STATES OF NF AT VARIOUS R

TABLE VI

INTERNUCLEAR DISTANCE (R) (ATOMIC UNITS)	TOTAL ENERGIES (ATOMIC UNITS)			
	NF X $^3\Sigma$	NF $^1\Delta$	NF$^+$ $^2\Pi$	NF$^+$ $^4\Pi$
2.00	-153.0760	-152.9849	-152.7468	-152.4587
2.20	-153.1754	-153.0842	-152.8141	-152.6454
2.25	-153.1877	-153.0965	-152.8194	-152.6773
2.30	-153.1963	-153.1051	-152.8214	-152.7048
2.35	-153.2011	-153.1101	-152.8197	-152.7282
2.40	-153.2044	-153.1135	-152.8175	-152.7484
2.45	-153.2046	-153.1138	-152.8121	-152.7653
2.50	-153.2026	-153.1120	-152.8049	-152.7793
2.55	-153.1991	-153.1087	-152.7965	-152.7911
2.60	-153.1939	-153.1039	-152.7866	-152.8007
2.80	-153.1619	-153.0740		-152.8224
2.85	-153.1508	-153.0638		-152.8235
2.90	-153.1398	-153.0538		-152.8248
2.95		-153.0432		-152.8242
3.00		-153.0329		-152.8235

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2.0675	-108.57509948	-108.31080437	-108.10986519	-108.29988861	-108.03031731	-107.84392548
2.4435	-108.52298260	-108.42863319	-108.08627224	-108.35072613	-108.02801609	-107.76351261
2.1699	-108.58127213	-108.36924934	-108.12618828	-108.36681107	-108.05045509	-107.84259796
2.2910	-108.56557846	-108.40950012	-108.12010384	-108.35496712	-108.05101776	-107.81772614
2.1094	-108.58209973	-108.33788681	-108.11937714	-108.31785011	-108.04117966	-107.84600639
2.0315	-108.56740284	-108.28355122	-108.09807873	-108.28082180	-108.01760006	-107.83875751

TABLE II - TOTAL ENERGIES OF DIFFERENT STATES OF CO MOLECULE AT VARIOUS INTERNUCLEAR DISTANCES

R	$^3\Pi$ (CO)	$^3\Delta$ (CO)	$X\,^1\Sigma$ (CO)	$C\,^2\Sigma$ (CO⁺)	$X\,^2\Sigma$ (CO⁺)	$A\,^2\Pi$ (CO⁺)	$B\,^2\Sigma$ (CO⁺)
1.90	-111.97424603		-115.23902798		-111.78087902		-111.42243862
1.95	-112.01778221	-111.89608574	-112.29486847		-111.81227303		-111.45487213
2.00	-112.05291748	-111.94694138	-112.31681442	-110.78995514	-111.83583450		-111.47964859
2.05	-112.08070755	-111.99008560	-112.33207321	-110.83036613	-111.85273170		-111.49787331
2.10	-112.10238266	-112.02656937	-112.34168434	-110.86468315	-111.86396408	-111.78398895	-111.51057243
2.15	-112.11864948	-112.05714130	-112.34640408	-110.89357662	-111.87039852	-111.80711269	-111.51859188
2.20	-112.13039207	-112.08272362	-112.34704590	-110.91785812	-111.87287712	-111.82560539	-111.52266884
2.25	-112.13831711	-112.10388184	-112.34418869	-110.93803787	-111.87201118	-111.84011650	-111.52353287
2.30	-112.14987376	-112.12103271	-112.33818436	-110.95444298	-111.86835098	-111.85105324	-111.52169418
2.35	-112.14478807	-112.13495731	-112.32978153	-110.96789074	-111.86255360	-111.85912228	-111.51773167
2.40	-112.14426422	-112.14583397	-112.31918526	-110.97831154	-111.85496330	-111.86448479	-111.51213264
2.45	-112.14194870	-112.15419960	-112.30690193	-110.98631859	-111.84608841	-111.86773300	-111.50533485
2.50	-112.13806438	-112.16026592	-112.29314895	-110.99185658	-111.83613110	-111.86907482	-111.49762440
2.55	-112.13303375	-112.16435432	-112.27814102	-110.99520874	-111.82550240	-111.86875916	-111.48933601
2.60	-112.12682152	-112.16669083	-112.26219940	-110.99636650	-111.81435966	-111.86703491	-111.48070717
2.65	-112.11972904	-112.16752929	-112.24554920	-110.99544621	-111.80296421	-111.86421871	-111.47183132
2.70	-112.11221027	-112.16697788	-112.22819042	-110.99233150	-111.79129505	-111.86032772	-111.46261311
2.75		-112.16510201	-112.21033096	-110.98709869	-111.77958488	-111.85550777	-111.45306969
2.80		-112.16249371	-112.19238758	-110.98032475	-111.76816273	-111.85039997	-111.44330311
2.85		-112.15889549	-112.17424583	-110.97213364	-111.75688362	-111.84469986	-111.43299675

TABLE III

EQUILIBRIUM DIATANCES (Re) OF THE VARIOUS ELECTRONIC STATES OF N_2 MOLECULE IN ATOMIC UNITS (a.u.)

STATE	EQUILIBRIUM DISTANCE		
	CALCULATED	OBSERVED	°/o ERROR
N_2 X $^1\Sigma_g^+$	2.15	2.0675	3.99°/o
A $^3\Sigma_u^+$	2.48	2.4435	1.49°/o
$^3\Pi_u$	2.20	2.1699	1.39°/o
$^3\Pi_g$	2.34	2.2910	2.14°/o
N_2^+ X $^2\Sigma_g^+$	2.23	2.1094	5.72°/o
B $^2\Sigma_u^+$	2.11	2.0315	3.86°/o

TABLE IV
EQUILIBRIUM DISTANCES OF THE VARIOUS ELECTRONIC STATES OF CO MOLECULE IN ATOMIC UNITS (a.u.)

STATE	EQUILIBRIUM DISTANCE		
	CALCULATED	OBSERVED	°/o ERROR
CO X $^1\Sigma^+$	2.18	2.132	2.25°/o
a $^3\Pi$	2.365	2.2853	3.49°/o
d $^3\Delta$	2.65	2.5888	2.36°/o
CO^+ X $^2\Sigma^+$	2.21	2.1072	4.87°/o
A $^2\Pi_1^+$	2.51	2.3502	6.79°/o
B $^2\Sigma^+$	2.24	2.2085	1.42°/o
c $^2\Sigma^+$	2.60	——	——

NF X $^3\Sigma$: $1\sigma^2$ $2\sigma^2$ $3\sigma^2$ $4\sigma^2$ $5\sigma^2$ Π_x^2 Π_y^2 Π_x^* Π_y^*

NF $^1\Delta$: $1\sigma^2$ $2\sigma^2$ $3\sigma^2$ $4\sigma^2$ $5\sigma^2$ Π_x^2 Π_y^2 Π_x^{*2}

NF$^+$ $^2\Pi$: $1\sigma^2$ $2\sigma^2$ $3\sigma^2$ $4\sigma^2$ $5\sigma^2$ Π_x^2 Π_y^2 Π_x^*

NF$^+$ $^4\Pi$: $1\sigma^2$ $2\sigma^2$ $3\sigma^2$ $4\sigma^2$ $5\sigma^2$ Π_x^2 Π_x Π_x^* Π_y^*

The computed total energies of the states of O_2 are given in Table V and those of NF in Table VI. The calculated equilibrium distances from the above data are given in Table VII for states of O_2 molecule along with observed data.

The predicted equilibrium distances of the states of NF along with excitation and ionization energies are given in Table VIII. The above results are preliminary. A more complete study using the best MO's (where both the linear coefficients and orbital exponents are varied) is under way. The complete results will be described in the next report.

(3) DEVELOPMENT OF THE COMPUTER PROGRAM FOR THE VARIATION OF THE SCREENING CONSTANTS OF THE 1s, 2s AND 2p ATOMIC ORBITALS TO OBTAIN BEST LCAO MO'S FOR THE DIFFERENT ELECTRONIC STATES OF DIATOMIC HOMOPOLAR MOLECULES
by R. C. Sahni and C. D. La Budde

It was stated in the previous report that an automatic program has been built up which computes wave functions and total energies of homopolar diatomic molecules. This program can compute six to seven states of the same molecule in 3 - 4 minutes in a single run. The program uses fixed screening constants as an input data. It is usual to use Slater screening constants. In order to get the best wave functions and total energies it is necessary to vary the screening constants to optimize the total energy. Such a program has been constructed and a number of states of N_2 and O_2 have been computed. The total energies of these states are given in Table IX along with those computed by using only Slater's screening constants. In all cases best LCAO MO's give better results.

(4) DEVELOPMENT OF THE COMPUTER PROGRAMS FOR THE VARIATION OF THE SCREENING CONSTANTS OF THE 1s, 2s AND 2p ATOMIC ORBITALS TO OBTAIN BEST LCAO MO'S FOR THE DIFFERENT ELECTRONIC STATES OF DIATOMIC HETEROPOLAR MOLECULES
by C. D. La Budde and R. C. Sahni

An 'auto vary' program has been built up which varies the screening constants of the different atomic orbitals of heteropolar molecules till the optimized energy is obtained. This program is more complicated than a similar program for homopolar molecules. This program has been used to calculate the

TABLE V
TOTAL ENERGIES OF STATES OF O_2 MOLECULE AT VARIOUS R
$\alpha = 7.6528$ $\beta = \gamma = \delta = 2.275$

R	$O_2\ ^3\Sigma_g^-$	$O_2\ ^1\Delta$	$O_2\ ^4\Pi$	$O_2\ ^2\Pi$
2.00	-149.02007866	-148.93554115	-148.48109627	-148.66397476
2.05	-149.04732704	-148.96336937	-148.53122520	-148.68243599
2.10	-149.06742668	-148.98403314	-148.57303238	-148.69430542
2.15	-149.08137894	-148.99849701	-148.60758781	-148.70056343
2.20	-149.09014702	-149.00779533	-148.63587379	-148.70213509
2.25	-149.09440804	-149.01255989	-148.65663800	-148.69966125
2.30	-149.09491158	-149.01353455	-148.67663765	-148.69385719
2.35	-149.09214592	-149.01122856	-148.69046211	-148.68519783
2.40	-149.08661842	-149.00615120	-148.70061684	-148.67414665
2.45	-149.07877731	-148.99873161	-148.70763397	-148.66114235
2.50	-149.06890488	-148.98927879	-148.71180344	-148.64645576
2.55	-149.05746460	-148.97822571	-148.71364784	-148.63051987
2.60	-149.04456902	-148.96571732	-148.71332932	-148.61343002
2.65	-149.03048897	-148.95200157	-148.71114159	-148.59544945
2.70	-149.01558113	-148.93743706	-148.70748901	-148.57689476
2.28170	-149.09510422	-149.01355362	-148.67054176	-148.69631004
2.29705	-149.09498596	-149.01357651	-148.67571831	-148.69429779
2.12163	-149.07416344	-148.99098587	-148.58880615	-148.69765663
2.61025	-149.04183960	-148.96305084	-148.71307755	-148.60987091

TOTAL ENERGIES OF STATES OF NF AT VARIOUS R

TABLE VI

INTERNUCLEAR DISTANCE (R) (ATOMIC UNITS)	TOTAL ENERGIES (ATOMIC UNITS)			
	NF X $^3\Sigma$	NF $^1\Delta$	NF$^+$ $^2\Pi$	NF$^+$ $^4\Pi$
2.00	-153.0760	-152.9849	-152.7468	-152.4587
2.20	-153.1754	-153.0842	-152.8141	-152.6454
2.25	-153.1877	-153.0965	-152.8194	-152.6773
2.30	-153.1963	-153.1051	-152.8214	-152.7048
2.35	-153.2011	-153.1101	-152.8197	-152.7282
2.40	-153.2044	-153.1135	-152.8175	-152.7484
2.45	-153.2046	-153.1138	-152.8121	-152.7653
2.50	-153.2026	-153.1120	-152.8049	-152.7793
2.55	-153.1991	-153.1087	-152.7965	-152.7911
2.60	-153.1939	-153.1039	-152.7866	-152.8007
2.80	-153.1619	-153.0740		-152.8224
2.85	-153.1508	-153.0638		-152.8235
2.90	-153.1398	-153.0538		-152.8248
2.95		-153.0432		-152.8242
3.00		-153.0329		-152.8235

TABLE VII

EQUILIBRIUM DISTANCES OF THE VARIOUS STATES OF

O_2 MOLECULE IN ATOMIC UNITS (a.u.)

STATE	EQUILIBRIUM DISTANCE (a.u.)		
	CALCULATED	OBSERVED	% ERROR
$O_2 \quad X \, ^3\Sigma_g^-$	2.28	2.28170	—
$a \, ^1\Delta_g$	2.29	2.29705	—
$O_2^+ \quad X \, ^2\Pi_g$	2.19	2.1216	3.22%
$a \, ^4\Pi_u$	2.57	2.6103	1.54%

TABLE VIII

PREDICTED EQUILIBRIUM DISTANCES OF THE VARIOUS STATES

OF NF MOLECULE ALONG WITH PREDICTED IONIZATION AND

EXCITATION ENERGIES

STATE	CALCULATED EQUILIBRIUM DISTANCES (a.u.)	VERTICAL IONIZATION AND EXCITATION ENERGIES (eV)
$NF \quad ^3\Sigma$	2.44	—
$^1\Delta$	2.43	2.47
$NF^+ \quad ^2\Pi$	2.30	10.65
$^4\Pi$	2.89	12.04

TOTAL ENERGIES AS WELL AS IONIZATION AND EXCITATION
ENERGIES OF THE DIFFERENT STATES OF N_2 AND O_2
MOLECULES AT R=2.0675 a.u. AND R=2.28167 a.u.
RESPECTIVELY

TABLE IX

	TOTAL ENERGIES IN (a.u.)		IONIZATION OR EXCITATION ENERGIES IN e.V.		
STATES	SLATER'S SET	BEST LCAO MO's	SLATER'S SET	BEST LCAO MO's	OBSERVED
N_2 $^1\Sigma_g^+$	-108.5736	-108.6335	—	—	—
A $^3\Sigma_u^+$	-108.3091	-108.3665	7.19	7.265	7.70
B $^3\Pi_g$	-108.2983	-108.3357	8.103	8.21	8.12
c $^3\Pi_u$	-108.1085	-108.1587	12.92	12.78	11.25
N_2^+ X$^2\Sigma_g^+$	-108.0294	-108.0762	15.16	15.81	15.576
X$^2\Sigma_u^+$	-107.8432	-107.9207	19.40	19.99	18.72
O_2 X$^3\Sigma_g^-$	-149.0921	-149.1173	—	—	—
a $^1\Delta_g$	-149.0105	-149.0375	2.22	2.17	1.0
O_2^+ X $^2\Pi_g$	-148.6941	-148.7116	11.04	11.93	12.2
a $^4\Pi_u$	-148.6682	-148.6707	12.15	13.07	16.1

TOTAL ENERGIES AS WELL AS IONIZATION AND EXCITATION
ENERGIES OF THE DIFFERENT STATES OF CO, NO AND CN
MOLECULES AT R = 2.132 a.u., R = 2.17472 a.u.
AND R = 2.21441 a.u. RESPECTIVELY

TABLE X

STATES	TOTAL ENERGIES IN (a.u.)		IONIZATION OR EXCITATION ENERGIES IN e.V.		
	SLATER'S SET	BEST LCAO MO's	SLATER'S SET	BEST LCAO MO'S	OBSERVED
CO X $^1\Sigma^+$	-112.3436	-112.3924	—	—	—
a $^3\Pi$	-112.1118	-112.1438	6.31	6.76	6.33
d $^3\Delta$	-112.0450	-112.0923	8.12	8.16	9.55
CO$^+$ X $^2\Sigma^+$	-111.8676	-111.9070	12.95	13.21	14.00$_9$
A $^2\Pi$	-111.7982	-111.8662	14.84	14.32	16.58
B $^2\Sigma$	-111.5152	-111.5556	22.54	22.77	19.69
C $^2\Sigma$	-110.8832	-110.9446	39.73	39.396	
NO X $^2\Pi$	-128.7983	-128.8401	—	—	—
NO$^+$ X $^1\Sigma^+$	-128.4772	-128.5286	8.74	8.476	9.25
CN X $^2\Sigma$	- 91.9108	- 91.9500			
A $^2\Pi$	- 91.8924	- 91.9338	.501	.440	1.30
CN$^+$ X $^1\Sigma$	- 91.3744	- 91.3917	14.595	15.191	
CN$^-$ X $^1\Sigma$	- 91.9147	—	-.106	—	—

total energies of a number of states of CO, NO and CN. The results are given in Table X along with those calculated by using Slater's screening. In all cases best LCAO MO's give better results.

(5) THE POTENTIAL ENERGY CURVES AND VIBRATIONAL WAVE FUNCTIONS OF DIATOMIC MOLECULES
by D. C. Jain

(a) Rydberg-Klein-Rees Potential Energy Curves

The RKR method is very useful for calculating the realistic potential energy curves of diatomic molecules. The approximate expressions given by Singh and Jain (1962a) are quite convenient to use and are known to yield sufficiently accurate and consistent results. This is apparent from the results published by Singh and Jain (1962b,c;1964a,b). Thus a program RKR MHHL XP has been written for calculating the RKR curves by using Singh and Jain's expressions. The program computes the RKR curves from experimental data and compares them graphically with the Morse, the Hulburt-Hirschfelder and the Lippincott functions. Thus the performance of these potential functions can be checked and the relative positions of the RKR potential curves with respect to these potential functions determined. However, the method of numerical integration of Klein's equations is the most accurate one for obtaining the RKR curves. Therefore, two programs have been constructed for the purpose. One of them (RKV) uses the technique suggested by Weissman, Vanderslice and Battino (1963) for avoiding the singularity in the original equations and the other one (RKG) uses the technique of Guassian integration in the vicinity of the singularity.

The program RKR MHHL XP has been used for computing the potential energy curves of various electronic states of alkali molecules and of C_2 molecule. The programs RKV and RKG have been checked by calculating the potential energy curves of the $X {}^1 \Sigma_g^+$ state of H_2, $X {}^1 \Sigma_g^+$ state of N_2 and $B {}^3 \Sigma_u^-$ state of O_2 molecule and it has been found that the results obtained by the two methods are in good agreement.

(b) Vibrational Wave Functions Appropriate to RKR Potential Energy Curves

Jain and Sah (1962) and Jain (1964b) found that the WKB method yields sufficiently accurate vibrational wave functions. Thus a program PSI VIB TP has been written for computing the vibrational wave functions appropriate to the RKR potential energy curves. It uses the WKB expressions. The solutions involving the Bessel functions are used in the region of the turning points. The wave functions are plotted by the SC 4020 machine. These are used for calculating the rotational constant B_v for various vibrational levels. These results can then be compared with

the experimental values of B_v. Preliminary results indicate that in the case of the $X\,^1\Sigma_g^+$ state of N_2 the values of B_v obtained by this procedure agree to about 0.2°/o with the experimental ones.

A slightly modified form of this program is available which can be used for obtaining the values of the vibrational and rotational constants using the theoretical potential energy curves calculated from first principles.

(c) Vibrational Wave Functions Appropriate to the Morse, the Hulburt-Hirschfelder and the Lippincott Functions

The Morse, the Hulburt-Hirschfelder or the Lippincott potential energy functions may be found to be quite adequate for representing the potential energy curves of certain electronic states. Thus it would be more convenient to use these potential functions for obtaining the vibrational wave functions in those cases. The program PSI VIB WKB has been constructed with this end in view. It calculates the vibrational wave functions appropriate to these potential functions and plots them using the SC4020 machine. These wave functions will be useful for computing the Franck-Condon factors and r-centroids for the band systems involving such electronic states whose potential energy curves can be adequately represented by any of these potential energy functions.

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TABLE VII

EQUILIBRIUM DISTANCES OF THE VARIOUS STATES OF

O_2 MOLECULE IN ATOMIC UNITS (a.u.)

STATE	EQUILIBRIUM DISTANCE (a.u.)		
	CALCULATED	OBSERVED	% ERROR
O_2 $X\ ^3\Sigma_g^-$	2.28	2.28170	——
$a\ ^1\Delta_g$	2.29	2.29705	——
O_2^+ $X\ ^2\Pi_g$	2.19	2.1216	3.22%
$a\ ^4\Pi_u$	2.57	2.6103	1.54%

TABLE VIII

PREDICTED EQUILIBRIUM DISTANCES OF THE VARIOUS STATES

OF NF MOLECULE ALONG WITH PREDICTED IONIZATION AND

EXCITATION ENERGIES

STATE	CALCULATED EQUILIBRIUM DISTANCES (a.u.)	VERTICAL IONIZATION AND EXCITATION ENERGIES (eV)
NF $^3\Sigma$	2.44	——
$^1\Delta$	2.43	2.47
NF$^+$ $^2\Pi$	2.30	10.65
$^4\Pi$	2.89	12.04

TOTAL ENERGIES AS WELL AS IONIZATION AND EXCITATION
ENERGIES OF THE DIFFERENT STATES OF N_2 AND O_2
MOLECULES AT R=2.0675 a.u. AND R=2.28167 a.u.
RESPECTIVELY

TABLE IX

STATES	TOTAL ENERGIES IN (a.u.)		IONIZATION OR EXCITATION ENERGIES IN e.V.		
	SLATER'S SET	BEST LCAO MO's	SLATER'S SET	BEST LCAO MO's	OBSERVED
N_2 $^1\Sigma_g^+$	-108.5736	-108.6335	—	—	—
A $^3\Sigma_u^+$	-108.3091	-108.3665	7.19	7.265	7.70
B $^3\Pi_g$	-108.2983	-108.3357	8.103	8.21	8.12
C $^3\Pi_u$	-108.1085	-108.1587	12.92	12.78	11.25
N_2^+ $x^2\Sigma_g^+$	-108.0294	-108.0762	15.16	15.81	15.576
$x^2\Sigma_u^+$	-107.8432	-107.9207	19.40	19.99	18.72
O_2 $x^3\Sigma_g^-$	-149.0921	-149.1173	—	—	—
a $^1\Delta_g$	-149.0105	-149.0375	2.22	2.17	1.0
O_2^+ x $^2\Pi_g$	-148.6941	-148.7116	11.04	11.93	12.2
a $^4\Pi_u$	-148.6682	-148.6707	12.15	13.07	16.1

TOTAL ENERGIES AS WELL AS IONIZATION AND EXCITATION
ENERGIES OF THE DIFFERENT STATES OF CO, NO AND CN
MOLECULES AT R = 2.132 a.u., R = 2.17472 a.u.
AND R = 2.21441 a.u. RESPECTIVELY

TABLE X

STATES	TOTAL ENERGIES IN (a.u.)		IONIZATION OR EXCITATION ENERGIES IN e.V.		
	SLATER'S SET	BEST LCAO MO's	SLATER'S SET	BEST LCAO MO'S	OBSERVED
CO X $^1\Sigma^+$	-112.3436	-112.3924	—	—	—
a $^3\Pi$	-112.1118	-112.1438	6.31	6.76	6.33
d $^3\Delta$	-112.0450	-112.0923	8.12	8.16	9.55
CO$^+$ X $^2\Sigma^+$	-111.8676	-111.9070	12.95	13.21	14.00$_9$
A $^2\Pi$	-111.7982	-111.8662	14.84	14.32	16.58
B $^2\Sigma$	-111.5152	-111.5556	22.54	22.77	19.69
C $^2\Sigma$	-110.8832	-110.9446	39.73	39.396	
NO X $^2\Pi$	-128.7983	-128.8401	—	—	—
NO$^+$ X $^1\Sigma^+$	-128.4772	-128.5286	8.74	8.476	9.25
CN X $^2\Sigma$	- 91.9108	- 91.9500			
A $^2\Pi$	- 91.8924	- 91.9338	.501	.440	1.30
CN$^+$ X $^1\Sigma$	- 91.3744	- 91.3917	14.595	15.191	
CN$^-$ X $^1\Sigma$	- 91.9147	—	-.106	—	—

total energies of a number of states of CO, NO and CN. The results are given in Table X along with those calculated by using Slater's screening. In all cases best LCAO MO's give better results.

(5) **THE POTENTIAL ENERGY CURVES AND VIBRATIONAL WAVE FUNCTIONS OF DIATOMIC MOLECULES**

by D. C. Jain

(a) Rydberg-Klein-Rees Potential Energy Curves

The RKR method is very useful for calculating the realistic potential energy curves of diatomic molecules. The approximate expressions given by Singh and Jain (1962a) are quite convenient to use and are known to yield sufficiently accurate and consistent results. This is apparent from the results published by Singh and Jain (1962b,c;1964a,b). Thus a program RKR MHHL XP has been written for calculating the RKR curves by using Singh and Jain's expressions. The program computes the RKR curves from experimental data and compares them graphically with the Morse, the Hulburt-Hirschfelder and the Lippincott functions. Thus the performance of these potential functions can be checked and the relative positions of the RKR potential curves with respect to these potential functions determined. However, the method of numerical integration of Klein's equations is the most accurate one for obtaining the RKR curves. Therefore, two programs have been constructed for the purpose. One of them (RKV) uses the technique suggested by Weissman, Vanderslice and Battino (1963) for avoiding the singularity in the original equations and the other one (RKG) uses the technique of Guassian integration in the vicinity of the singularity.

The program RKR MHHL XP has been used for computing the potential energy curves of various electronic states of alkali molecules and of C_2 molecule. The programs RKV and RKG have been checked by calculating the potential energy curves of the $X\ ^1\Sigma_g^+$ state of H_2, $X\ ^1\Sigma_g^+$ state of N_2 and $B\ ^3\Sigma_u^-$ state of O_2 molecule and it has been found that the results obtained by the two methods are in good agreement.

(b) Vibrational Wave Functions Appropriate to RKR Potential Energy Curves

Jain and Sah (1962) and Jain (1964b) found that the WKB method yields sufficiently accurate vibrational wave functions. Thus a program PSI VIB TP has been written for computing the vibrational wave functions appropriate to the RKR potential energy curves. It uses the WKB expressions. The solutions involving the Bessel functions are used in the region of the turning points. The wave functions are plotted by the SC 4020 machine. These are used for calculating the rotational constant B_v for various vibrational levels. These results can then be compared with

the experimental values of B_v. Preliminary results indicate that in the case of the $X\ ^1\Sigma_g^+$ state of N_2 the values of B_v obtained by this procedure agree to about 0.2% with the experimental ones.

A slightly modified form of this program is available which can be used for obtaining the values of the vibrational and rotational constants using the theoretical potential energy curves calculated from first principles.

(c) **Vibrational Wave Functions Appropriate to the Morse, the Hulburt-Hirschfelder and the Lippincott Functions**

The Morse, the Hulburt-Hirschfelder or the Lippincott potential energy functions may be found to be quite adequate for representing the potential energy curves of certain electronic states. Thus it would be more convenient to use these potential functions for obtaining the vibrational wave functions in those cases. The program PSI VIB WKB has been constructed with this end in view. It calculates the vibrational wave functions appropriate to these potential functions and plots them using the SC4020 machine. These wave functions will be useful for computing the Franck-Condon factors and r-centroids for the band systems involving such electronic states whose potential energy curves can be adequately represented by any of these potential energy functions.

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